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# Source-Dependent and Source-Independent Controls on Plutonium Oxidation State and Colloid Associations in Groundwater

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Plutonium (Pu) was characterized for its isotopic composition, oxidation states, and association with colloids in groundwater samples near disposal basins in F-Area of the Savannah River Site and compared to similar samples collected six years earlier. Two sources of Pu were identified, the disposal basins, which contained a  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic signature consistent with weapons grade Pu, and  $^{244}\text{Cm}$ , a cocontaminant that is a progenitor radionuclide of  $^{240}\text{Pu}$ .  $^{240}\text{Pu}$  that originated primarily from  $^{244}\text{Cm}$  tended to be appreciably more oxidized (Pu(V/VI)), less associated with colloids ( $\sim 1$  kDa –  $0.2$   $\mu\text{m}$ ), and more mobile than  $^{239}\text{Pu}$ , as suggested by our prior studies at this site. This is not evidence of isotope fractionation but rather “source-dependent” controls on  $^{240}\text{Pu}$  speciation which are processes that are not at equilibrium, i.e., processes that appear kinetically hindered. There were also “source-independent” controls on  $^{239}\text{Pu}$  speciation, which are those processes that follow thermodynamic equilibrium with their surroundings. For example, a groundwater pH increase in one well from 4.1 in 1998 to 6.1 in 2004 resulted in an order of magnitude decrease in groundwater  $^{239}\text{Pu}$  concentrations. Similarly, the fraction of  $^{239}\text{Pu}$  in the reduced Pu(III/IV) and colloidal forms increased systematically with decreases in redox condition in 2004 vs 1998. This research demonstrates the importance of source-dependent and source-independent controls on Pu speciation which would impact Pu mobility during changes in hydrological, chemical, or biological conditions on both seasonal and decadal time scales, and over short spatial scales. This implies more dynamic shifts in Pu speciation, colloids association, and transport in groundwater than commonly believed.

## Introduction

An estimated  $1.3 \times 10^{16}$  Bq of plutonium ( $\sim 4200$  kg of Pu using a  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio of 0.18) has been released to the environment as a result of nuclear testing, the development of nuclear weapons, reactor operations, and the nuclear

fuel cycle (1). One legacy of the Cold War Era processing of nuclear materials includes contamination of many billions of cubic meters of soils and groundwater at DOE sites. Thus, the task of managing, cleaning-up, and monitoring these sites is large, and decisions regarding remediation and stewardship at DOE sites require sound scientific advice and site-specific field programs to understand Pu transport in subsurface vadose and groundwater zones.

While many details of Pu geochemistry in the laboratory are understood, its fate in the natural environment is far more difficult to predict. This is because of a variety of factors, including the coupled interactions of ambient hydrological, geochemical, and biological processes that control the many possible chemical forms, or species, of Pu. Differences in Pu speciation, in particular oxidation state, result in its variable affinity for stationary and colloidal surfaces in the subsurface environment. Understanding Pu contaminant transport is also limited by insufficient and unreliable field data. This is due in part to the extremely low concentrations of Pu in the environment, making Pu detection and detailed speciation work challenging. Most spectroscopic techniques require micromolar ( $10^{-6}$  M) or greater concentrations to be effective, whereas environmental Pu concentrations are typically in the subnanomolar range ( $<10^{-9}$  M, i.e., solubility limited 2–5). Finally, there are inherent difficulties that must be overcome in order to sample true in situ conditions in the subsurface (6, 7).

A recent review of subsurface contaminant transport (8) noted several conflicting conclusions regarding colloid-associated transport of Pu in groundwater (also called colloid-facilitated transport). Evidence in favor of this pathway is either indirect (unexpected detection of contaminants far from sources) or based upon laboratory or modeling studies which only show the possibility that high Pu colloid-association may exist under field conditions. Field studies of colloid-associated transport are far fewer and show more variable or little colloid-associated transport. Novikov et al. (9) found that Pu was transported 4 km within  $\sim 55$  years in the Lake Karachai region in Mayak, Russia, which they attribute primarily to colloid-associated transport. This was based upon sampling 10 wells and identifying Pu on filterable solids from groundwater samples. Similarly, Penrose et al. (10) reported that essentially all the groundwater Pu recovered from a well 2.3 km from a point source (wastewater outfall) at the Los Alamos National Laboratory site was filterable.

Kersting et al. (11) reported that groundwater Pu collected 1.3 km from an underground nuclear test at the Nevada Test Site was primarily on colloids (i.e.,  $>99\%$  filterable in  $\sim 100$  kDa to  $1$   $\mu\text{m}$  size range). Importantly, they also demonstrated using  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratios that the Pu in these samples originated from the underground nuclear test and not from overland or atmospheric pathways. However, finding a contaminant distant from a point source is not sufficient to confirm colloid-associated transport. Wind-born dust and surface waters, not subsurface mobile colloids, were the primary far-field transport mechanisms for Pu at Rocky Flats (12).

Choppin (13) and others have used the term “source-dependent” to refer to environmental behavior of Pu that depends upon the specific Pu source. Such Pu species are not at thermodynamic equilibrium with their surroundings but remain in forms that are influenced by the source. One example is Pu associated with solids entrained in fallout from above ground nuclear weapons testing at Nevada which are preferentially deposited in deep ocean sediments, because they are less soluble in seawater than Pu fallout from high

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altitude testing (14–18). Another source-dependent effect to be discussed here is the production of  $^{240}\text{Pu}$  from the decay of  $^{244}\text{Cm}$  ( $t_{1/2} = 18.1$  years), resulting in more oxidized forms of  $^{240}\text{Pu}$  in groundwater (19).

“Source-independent” effects refer to those geochemical processes that are sufficiently rapid to permit Pu speciation to come to steady state. Source-independent effects for Pu commonly include changes in redox state, pH, or concentrations of inorganic or organic ligands (4, 13, 20–22). Thus hydrological, chemical, or biological changes in groundwater conditions on both seasonal and decadal time scales, and over short spatial scales, would be expected to influence source-independent Pu speciation.

The objective of this study was to evaluate changes in Pu speciation in the groundwater at the Savannah River Site (SRS) in the time since our previous sampling six years ago (19). Furthermore, attention was directed at explaining the systematic increases with distance from the source in  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio, which was inferred in prior sampling to be a consequence of the decay of  $^{244}\text{Cm}$ , a progenitor radionuclide of  $^{240}\text{Pu}$  (19). Therefore, this study also involved the first measurements of  $^{244}\text{Cm}$  in SRS groundwater.

## Experimental Section

**Study Site.** The SRS was constructed in the early 1950s in western South Carolina for the production of nuclear materials, mainly  $^3\text{H}$  and  $^{239}\text{Pu}$  for defense purposes and  $^{238}\text{Pu}$  and various transuranic radionuclides for medical, industrial, and scientific applications (23, 24). F-area seepage basins received waste effluents from the separation facilities, including waste from the nitric acid recovery unit and the evaporators that concentrated the dilute uranium nitrate solutions (25). For the most part, the groundwater flow direction is due south to southeast from the seepage basins toward Fourmile Branch, a second-order stream and tributary of the Savannah River (a map of the study site is presented in Supporting Information, Figure S1).

The same wells sampled by Dai et al. (19) in 1998 were resampled in 2004 including a “background” well located upstream of the seepage basins (Well 1) and three additional wells that formed a transect downstream of the seepage basins, Wells 2, 3, and 4, which are 10, 110, and 700 m, respectively, from the seepage basins. Since 2002, SRS has participated in a remediation effort which has injected 12 million liters of a sodium hydroxide–sodium bicarbonate solution into the groundwater for the purpose of increasing pH and increasing sediment sorption of plume contaminants (26, 27). The current remediation system consists of an impermeable barrier wall that funnels groundwater toward an opening gate where wells are used for base injection (so-called “funnel and gate”). Significant decreases in major contaminants (Cd, Hg, Ra,  $^{241}\text{Am}$ ,  $^{243,244}\text{Cm}$ ,  $^{90}\text{Sr}$ , and  $^{238}\text{U}$ ) have been measured (26, 27). Evidence of remedial activity was noted in this latest sampling at Well 4, located ~30 m downstream of the injection gate, where the pH increased from 4.1 in 1996 to as high as pH 6.5 in 2004 (see Supporting Information, Table S1). Significant changes in Pu solubility and speciation are expected to occur as a result of these pH changes. On the basis of laboratory measurements with SRS sediments, Pu solubility should decrease by 1 order of magnitude as the pH increases from 4.1 ( $10^{-7.8}$  M Pu) to 6.1 ( $10^{-8.8}$  M Pu) (5). On the basis of thermodynamic calculations of a sediment solution in contact with  $\text{PuO}_2(\text{s})$  in a mildly oxidizing soil environment ( $p\text{O}_2 = 16$  atm), the dominant Pu species at pH 4.1 are  $\text{PuO}_2^+$ ,  $\text{PuO}_2\text{CO}_3\text{OH}^-$ ,  $\text{PuO}_2(\text{OH})^0$ , and  $\text{PuO}_2^{2+}$ , whereas the dominant Pu species at pH 6.1 are  $\text{PuO}_2\text{CO}_3\text{OH}^-$ ,  $\text{PuO}_2\text{CO}_3(\text{OH})_2^{2-}$ , and  $\text{PuO}_2(\text{OH})_3^-$  (28).

**Field Sampling.** Part of the current confusion regarding Pu mobility in groundwater and more generally the role of colloids in facilitating contaminant transport is due to

sampling artifacts and biases that need to be carefully considered in the design of field studies (6, 7, 29, 30). For this reason, special attention was directed at sample collection and processing in the field. Our approach involved a combination of methods, including low flow rate groundwater sampling to minimize remobilizing Pu that would otherwise be stationary ( $\leq 150$  mL  $\text{min}^{-1}$ ) and directly sending the sample through a multimembrane, cross-flow ultrafiltration (CFF) assembly maintained in a  $\text{N}_2$  atmosphere (details in refs 19, 30, 31). In-line filtration (0.2  $\mu\text{m}$  filter) is used to ensure that no large particles enter the CFF system, though at low flow rates little difference between unfiltered and filtered Pu concentrations have been measured (19). Separation of the Pu oxidation state fractions was conducted immediately in the field. Strict protocols with respect to trace-metal and trace-organic clean sampling techniques were adopted during collection and field processing of samples. Details of the CFF method, redox controls, Pu oxidation state separations, and quality control on contamination and sorptive losses are presented in Supporting Information.

**Plutonium Isotopes by Thermal Ionization Mass Spectrometry.** Field samples underwent separation and purification in a clean laboratory as described in prior studies (19, 31) prior to thermal ionization mass spectrometry (TIMS) analyses. Pu isotopes were analyzed using a three-stage TIMS instrument at the Pacific Northwest National Laboratory (Dai et al., ref 19 and references therein). Sample aliquots seldom contained more than  $\sim 10^8$  Pu atoms; thus, most of the TIMS duty cycle was allocated to the measurement of the minor  $^{241}\text{Pu}$  and  $^{242}\text{Pu}$  isotopes. Given the TIMS duty cycle allocation, the detection limit was about  $10^4$  atoms, which is appreciably less than sample concentrations typically that were  $10^6 - 10^8$  atoms  $\text{kg}^{-1}$   $^{239}\text{Pu}$ .

**Curium Analysis.** New to this study was the direct determination of  $^{244}\text{Cm}$  by both alpha spectroscopy and TIMS methods. For alpha counting,  $^{243}\text{Am}$  was added as a yield tracer and the actinides were preconcentrated using a calcium phosphate coprecipitation method. Americium and curium were separated from the rest of the actinides by extraction chromatography on TRU resin (32). The purified Am and Cm isotopes were coprecipitated with cerium fluoride, filtered, and counted by alpha-spectrometry. SRS groundwater samples contain some  $^{243}\text{Am}$ , so a second set of samples were analyzed by alpha-spectrometry without yield tracer in order to calculate Am and Cm isotope ratios originally present in the sample. For the TIMS-based  $^{244}\text{Cm}$  method,  $^{248}\text{Cm}$  was added as a yield tracer and trivalent Cm was separated as an anionic thiocyanate complex by extraction chromatography using TEVA and analytical grade anion and cation exchange resins. Further purification and, ultimately, preparation of the TIMS source was accomplished using single anion exchange resin bead (Bio-Rad AG1-X4) which extracts the Cm(III) as an anionic nitrate complex in nonaqueous media. Following equilibration, the anion exchange resin bead was transferred to the trough of a rhenium filament and pyrolyzed and the filament carburized to produce the final TIMS source. Agreement between  $^{244}\text{Cm}$  determined from the same wells and dates by independent methods (1988, alpha counting, TIMS, ingrowth, Table 1) attests to the accuracy of these results.

## Results and Discussion

**$^{239}\text{Pu}$  Concentration, Oxidation State, and Colloidal Fraction.** Shown in Figure 1a–c are groundwater  $^{239}\text{Pu}$  data from the most recent field sampling in October 2004 compared to the same four wells sampled in April 1998 and reported in Dai et al. (19). All concentration data are presented in units of  $10^6$  atoms  $\text{kg}^{-1}$  ( $\sim 0.0065$  pCi  $\text{kg}^{-1}$  or 0.2 mBq  $\text{kg}^{-1}$  for  $^{239}\text{Pu}$ ). The drinking water limit for  $^{239}\text{Pu}$  is 15 pCi  $\text{L}^{-1}$  or

**TABLE 1. Comparison of Filtrate <sup>244</sup>Cm Concentrations Determined by Alpha Spectroscopy, TIMS, and Ingrowth Calculations**

well ID	<sup>244</sup> Cm (10 <sup>6</sup> atoms L <sup>-1</sup> )				ingrowth calculations <sup>a</sup> 1998
	alpha 2004 <sup>b</sup>	TIMS 2003	alpha 1998	TIMS 1998	
1	2 ± 11	-	-	<3	-
2	50 ± 24	180 ± 15	510 ± 130	560 ± 30	470
3	38 ± 14	-	1140 ± 440	1520 ± 120	800
4	9 ± 5	-	2630 ± 430	2320 ± 170	2750

<sup>a</sup> A more detailed description of estimating <sup>244</sup>Cm concentrations from ingrowth calculations based upon repeated measurements of <sup>240</sup>Pu is presented in Dai et al. (19). <sup>b</sup> Year of analysis or calculation.

50 000 × 10<sup>6</sup> atoms kg<sup>-1</sup>; the greatest Pu concentration measured in this study was 200 × 10<sup>6</sup> atoms kg<sup>-1</sup>.

Focusing first on the <sup>239</sup>Pu isotope and the measurement of Pu concentration in the filtrate (that which passes through a 0.2-μm filter, Figure 1a), in both 2004 and 1998 the greatest <sup>239</sup>Pu concentration was near the seepage basins, at Well 2 (140–170 × 10<sup>6</sup> atoms kg<sup>-1</sup>) and decreased rapidly downstream, in Wells 3 and 4. The background well had a measurable <sup>239</sup>Pu concentration of only 0.14 and 0.22 × 10<sup>6</sup> atoms kg<sup>-1</sup> in 1998 and 2004, respectively. One conclusion is that this pattern of sharp <sup>239</sup>Pu concentration decrease with distance from the source has not changed significantly during this 6-year period. However, there were more subtle but measurable increases in <sup>239</sup>Pu for Well 2 in 2004 (170 × 10<sup>6</sup> atoms kg<sup>-1</sup>) versus 1998 (140 × 10<sup>6</sup> atoms kg<sup>-1</sup>) and for Well 3 in 2004 (10 × 10<sup>6</sup> atoms kg<sup>-1</sup>) versus 1998 (5 × 10<sup>6</sup> atoms kg<sup>-1</sup>), and a small decrease in <sup>239</sup>Pu in Well 4 in 2004 (1 × 10<sup>6</sup> atoms kg<sup>-1</sup>) versus in 1998 (4 × 10<sup>6</sup> atoms kg<sup>-1</sup>). Among the possible explanations for the decrease of <sup>239</sup>Pu in Well 4 is that it is downstream of the base injection remediation point (Figure S1, Supporting Information), which may have promoted greater sediment sorption.

The largest differences in <sup>239</sup>Pu between 2004 and 1998 were not in concentration but in the percentage of Pu in the reduced form (Figure 1b). The reduced fraction included Pu(III) and Pu(IV) but was likely dominated by Pu(IV) (33–37). Conversely, the oxidized fraction included Pu(V) and Pu(VI), but was likely dominated by Pu(V) (34, 38, 39). While the same overall pattern existed in 2004 and 1998, namely, Well 3 contained the largest fraction of reduced Pu, followed by Well 4, the reduced fractions of the <sup>239</sup>Pu filtrate were appreciably greater in 2004. This data shows that oxidation state, the single most important parameter influencing the biogeochemical behavior of Pu (4, 20–22), had shifted appreciably between years and differed between wells within a single plume. With this increase in percent reduced Pu downstream in 2004, in general, an increase in colloidal <sup>239</sup>Pu was also measured, though not in Well 2 (Figure 1c). Colloidal <sup>239</sup>Pu increased to 20% in both Wells 3 and 4. In 1998, there was <5% colloidal <sup>239</sup>Pu; however, Wells 3 and 4 had measurably higher colloidal Pu concentrations than Wells 1 and 2.

In summary, the 2004 samples had a sharp decrease in <sup>239</sup>Pu concentrations downstream from the source, along with a shift to more reduced species and higher colloidal fractions. Batch sorption tests in the laboratory with SRS sediments showed that reduced Pu(IV) had distribution coefficients (*K<sub>d</sub>* values); the concentration ratio of sediment Pu to solution Pu) 2 orders of magnitude greater than oxidized Pu(V) for these sediments (40).

**Source-Dependent Controls on Pu Speciation.** <sup>240</sup>Pu had vastly different trends of concentration, oxidation state, and

colloidal fraction than <sup>239</sup>Pu. Immediately evident by comparison of Figures 1b and 1d is the difference in Pu oxidation state, such that the oxidized fraction of <sup>240</sup>Pu in all wells was much higher than for <sup>239</sup>Pu. In agreement with this finding, the colloidal fraction of <sup>240</sup>Pu is lower than that for <sup>239</sup>Pu, though still detectable downstream, in Wells 3 and 4 (Figures 1c and 1e). Dai et al. (19) postulated that the difference in the isotope trends in the 1998 data may be the result of source-dependent control on <sup>240</sup>Pu speciation, namely the decay of <sup>244</sup>Cm to <sup>240</sup>Pu. <sup>244</sup>Cm was produced at SRS and the Oak Ridge National Laboratory for use in experimental programs as a heat source for isotopic electrical power generators (41, 42), and by 1968 approximately 5 kg had been produced at SRS. With an 18.1 year half-life and several decades since its release, it has the ability to serve as a primary <sup>240</sup>Pu source in SRS groundwater (<sup>243</sup>Cm was also released, but at much lower levels that are insignificant for <sup>239</sup>Pu concentrations here). Cm is expected to be significantly more mobile in groundwater than Pu, based on its lower *K<sub>d</sub>*, or affinity for particle surfaces (43). Dai et al. (19) estimated, based on ingrowth calculations, that groundwater <sup>244</sup>Cm concentrations were as high as 2750 × 10<sup>6</sup> atoms kg<sup>-1</sup> in Well 4 (Table 1), thus 2–3 orders of magnitude higher than Pu in that well. Furthermore, they estimated that 99.5% of the <sup>240</sup>Pu in Well 4 originated from the decay of <sup>244</sup>Cm rather than from direct transport of <sup>240</sup>Pu originating from the seepage basins (19).

The <sup>244</sup>Cm results using TIMS and alpha-based methods show good agreement with values estimated based on ingrowth (Table 1), and a decrease in concentration of <sup>244</sup>Cm after treatment began between the two sampling campaigns. These <sup>244</sup>Cm data suggest that the sharp decrease in <sup>240</sup>Pu concentrations between the 1998 and 2004 samples were due to a large decrease in <sup>244</sup>Cm concentrations, especially in the treated Well 4 (1998 sample contained >2300 × 10<sup>6</sup> atoms kg<sup>-1</sup>, 2004 samples contained 9 × 10<sup>6</sup> atoms kg<sup>-1</sup>).

Why is there this source-dependent Pu isotope difference not only in concentration but also in Pu oxidation state and colloid fraction? We contend, and <sup>240</sup>Pu/<sup>239</sup>Pu and <sup>244</sup>Cm data confirm, that Pu produced from <sup>244</sup>Cm decay is significantly more oxidized, which we attribute to the production of <sup>240</sup>Pu via an electron-stripping Szilard–Chalmers process (44). The best evidence of this preferential formation and stabilization of the <sup>240</sup>Pu in the oxidized forms is seen in the isotopic composition of separated oxidized and reduced Pu fractions (Figure 2a). Looking at 2004 data, the reduced form of Pu has a <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio of 0.05–0.06 (Wells 1 and 2 in 2004) to 0.15 (Wells 3 and 4 in 2004) (Figure 2a). Weapons grade Pu is characterized by a low <sup>240</sup>Pu content, with <sup>240</sup>Pu/<sup>239</sup>Pu ratios usually <0.07 (45). Average SRS materials have ratios <0.05 to 0.15, related to weapons production and reactor operations, while global fallout from weapons testing has a very constant ratio near 0.18 in soils (46, 47). Given these expected <sup>240</sup>Pu/<sup>239</sup>Pu ratios, it is extraordinary to measure <sup>240</sup>Pu/<sup>239</sup>Pu ratios of 8–9 in Wells 3 and 4 for the oxidized filtrate fraction (Figure 2a). Note the reduced fraction maintained a low <sup>240</sup>Pu/<sup>239</sup>Pu ratio of <0.17 (Figure 2a). Clearly this indicates a source that is specific to the enrichment of <sup>240</sup>Pu in more oxidized form. Size-fractionated Cm data from 1998 and 2004, where >90% of the Cm was in the dissolved phase (<1 kDa; data not shown), support the interpretation of <sup>244</sup>Cm decay being the source of enriched oxidized <sup>240</sup>Pu and that the <sup>244</sup>Cm was highly mobile. If the concentration of each isotope is normalized to Well 2, it becomes even more obvious that the drop off in <sup>239</sup>Pu concentrations is much sharper than in <sup>240</sup>Pu concentrations (Figure 2b).

Detection of <sup>244</sup>Cm in SRS groundwater is not new (19); however, this suggestion is now confirmed by these direct Cm measurements. Importantly, this is not isotope fractionation but a source-dependent effect that enriches some

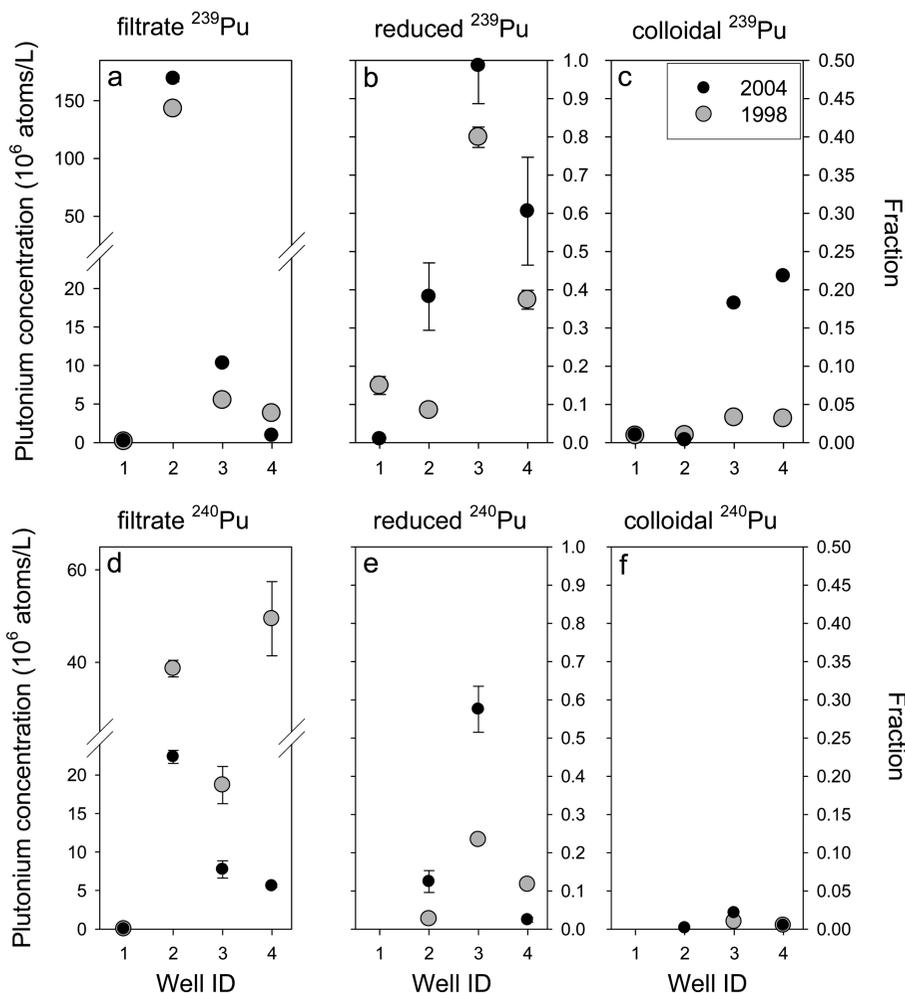


FIGURE 1. Comparison of  $^{239}\text{Pu}$  (a) concentrations, (b) fraction reduced, and (c) fraction colloidal in filtrate samples (<math><0.2 \mu\text{m}</math>) from October 2004 (black circles) and April 1998 (gray circles). Comparison of  $^{240}\text{Pu}$  (d) concentrations, (e) fraction reduced, and (f) fraction colloidal in filtrate samples (<math><0.2 \mu\text{m}</math>).

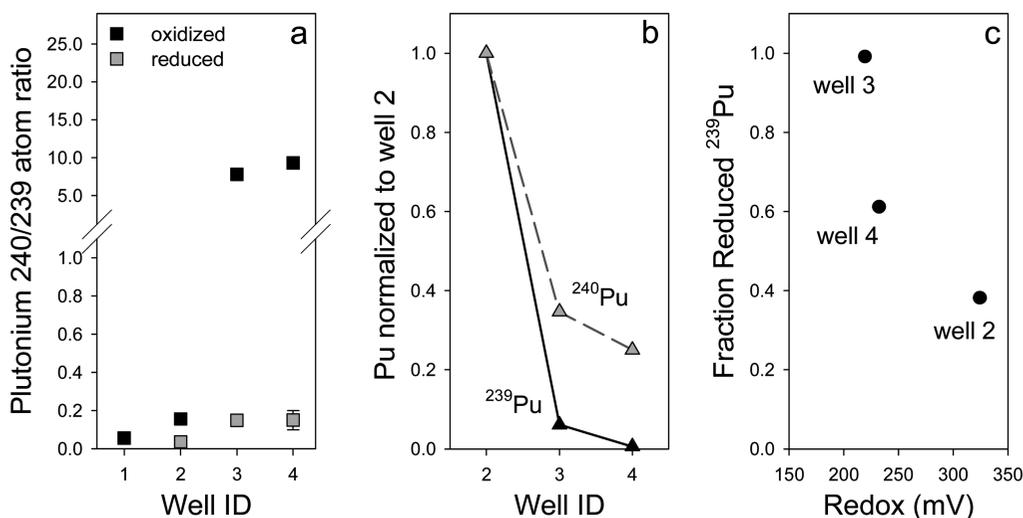
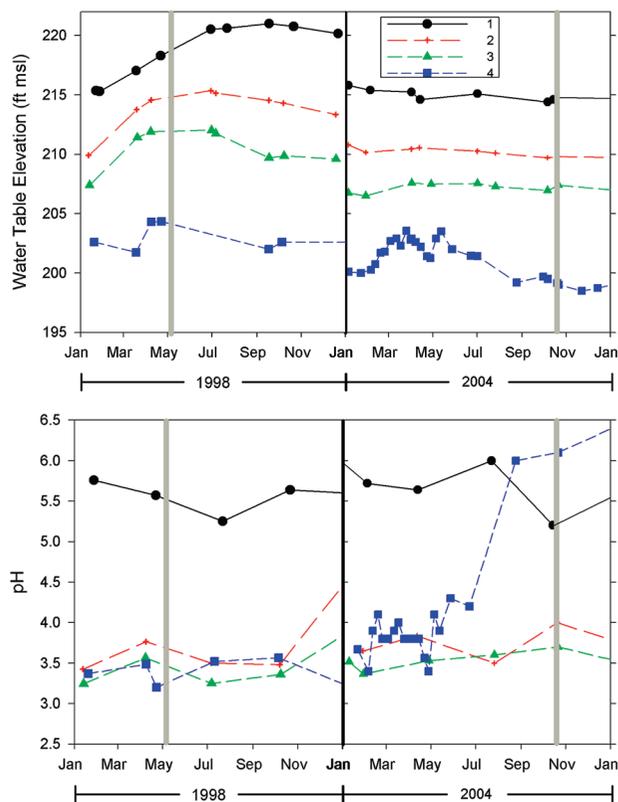


FIGURE 2. Comparison of data in 2004 on (a)  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in reduced (gray squares) and oxidized (black squares) fractions of filtrate (<math><0.2 \mu\text{m}</math>); (b) concentrations of filtrate  $^{239}\text{Pu}$  (black triangles) and  $^{240}\text{Pu}$  (gray triangles) normalized to Well 2 ( $^{240}\text{Pu}$  data have been corrected for ingrowth from  $^{244}\text{Cm}$  during storage); and (c) reduced fraction of  $^{239}\text{Pu}$  (0-1.0) vs redox potential (mV with respect to the standard hydrogen electrode) in filtrate fraction (<math><0.2 \mu\text{m}</math>) for Wells 2-4.

Pu isotopes over others. It should also be realized that the isotopic changes in groundwater Pu would not be detected with traditional alpha counting methods that do not distinguish between  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ .

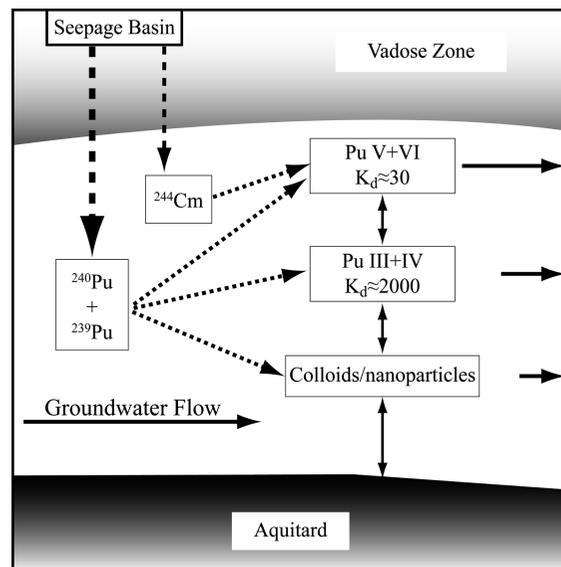
There were extremely large decreases in  $^{244}\text{Cm}$  concentration between the 1998 and 2004 samples and between wells within a given year (Table 1). The largest change by far is in the treated Well 4. Ames and Rai (48) reported that  $K_d$



**FIGURE 3.** (Upper panel) F-area water table elevations (ft above mean sea level) and (lower panel) pH for sampling years 1998 and 2004. Sampling periods for each site visit are represented as vertical gray bars in both years. Note shift to higher pH from 4 to 6 in 2004 in Well 4 is a result of NaOH/Na<sub>2</sub>CO<sub>3</sub> subsurface injections for site remediation efforts.

values of Cm had a strong pH dependence, increasing from 6803 mL/g at pH 2.6 to 100 000 at pH 5.6. Similarly, Cm  $K_d$  values of SRS sediment and groundwater were in the order of 40 mL g<sup>-1</sup> at pH 4 and 15 000 mL g<sup>-1</sup> at pH 6.7 (unpublished work by Kaplan, SRNL). Thus, the base injection remediation process is very likely promoting Cm precipitation or sorption to sediment, in particular at Well 4 where Cm concentrations have decreased by greater than 2 orders of magnitude, while Pu is only lowered by a factor of 4. Why <sup>244</sup>Cm is lower in 2004 at Wells 2 and 3 that are untreated is less clear.

**Source-Independent Controls on Pu Speciation.** Source-independent controls are indicated by the observed shift to greater colloidal Pu abundances for both isotopes in the wells which contain greater percentages of reduced Pu (Figures 1b and 1c and Figures 1e and 1f). Data consistent with this is the inverse relation between redox potential (as estimated by Eh) and fraction of reduced <sup>239</sup>Pu (Figure 2c). Water table height records show that our 1998 samples were collected during a period of greatly enhanced groundwater infiltration, a shift in roughly 2.3 m elevation over 6 months in each well (Figure 3), which is the largest shift measured in the 6 year period between 1998 and 2004. It is quite possible that this large “freshening” event was responsible for the more oxidizing condition in 1998, but there is insufficient ancillary data to establish whether other factors were also involved. Well pH data showed that changes of 0.5–1 log units were common (Figure 3). The sharp pH increase in Well 4 in May 2004 from pH 4 to 6 reflects a recent base injection as part of the remediation strategy (Figure 3). Pu speciation is particularly sensitive to pH in the range of pH 3–4 found in these acidic wells (5). If Pu speciation is changed after freshening events, then Pu transport may be episodic and missed with standard monitoring programs.



**FIGURE 4.** Schematic of proposed Pu sources, speciation, and transport mechanisms. Note SRS F-area seepage basins are both a direct source of <sup>239</sup>Pu and <sup>240</sup>Pu as well as <sup>244</sup>Cm. <sup>244</sup>Cm decays to <sup>240</sup>Pu predominantly in more oxidized forms with inherently lower affinities for the stationary porous media and mobile colloids surfaces, resulting in source-dependent fractionation of <sup>240</sup>Pu from <sup>239</sup>Pu. Temporal changes in groundwater chemistry are source-independent controls on Pu speciation.

#### Conceptual Model of Pu Sources, Speciation, and Transport.

The data collected here confirm that there are both source-dependent and source-independent controls on groundwater Pu in SRS F-area (Figure 4). The source-dependent control originates from the decay of <sup>244</sup>Cm to a highly mobile dissolved form of Pu, namely an oxidized, noncolloidal form of <sup>240</sup>Pu. The relative concentration of <sup>240</sup>Pu compared to <sup>239</sup>Pu tends to increase rapidly downstream of the disposal basins as a result of two simultaneous processes: (1) <sup>244</sup>Cm moves through the aquifer more readily than Pu and then decays to <sup>240</sup>Pu, releasing the <sup>240</sup>Pu further downstream; and (2) <sup>240</sup>Pu formed by the decay of <sup>244</sup>Cm tends to exist in an oxidized, noncolloidal form as a result of the electron stripping Szilard–Chalmers process. This transport mechanism involving <sup>244</sup>Cm accounts for 99.5% of the dissolved or colloidal Pu in groundwater away from the seepage basins. Source-independent controls, including pH and redox potential, influence Pu speciation in a manner consistent with thermodynamic considerations, but may have a secondary role when source-dependent controls are active.

To our knowledge, this is the first study to resample a field site and report changes in groundwater Pu speciation, including its association with colloids. The results show that Pu geochemistry is more dynamic and less kinetically hindered than commonly believed. Subtle changes in groundwater conditions occur over short distances (<1 km) and time scales that promote Pu speciation changes. An important implication of these findings is that it may be necessary to model the fate and transport of Pu with reactive transport models that capture the influence of changing groundwater geochemistry and, when present, progenitor radionuclides with source-dependent controls on Pu speciation.

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### Supporting Information Available

Figure S1: SRS F-area site map for Wells 1, 2, 3, 4; Table S1: Aqueous chemistry of unfiltered well water; a methods section: on site cross-flow filtration and maintaining in situ groundwater redox state, plutonium oxidation states, and consistency of results. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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## **Supplemental Information**

### **Source Dependent and Source Independent Controls on Plutonium Oxidation State and Colloid Associations in Groundwater**

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#### **Contents**

**Figure S1-** Location of the four wells sampled in this study

**Table S1-** Aqueous Chemistry of Unfiltered Well Water

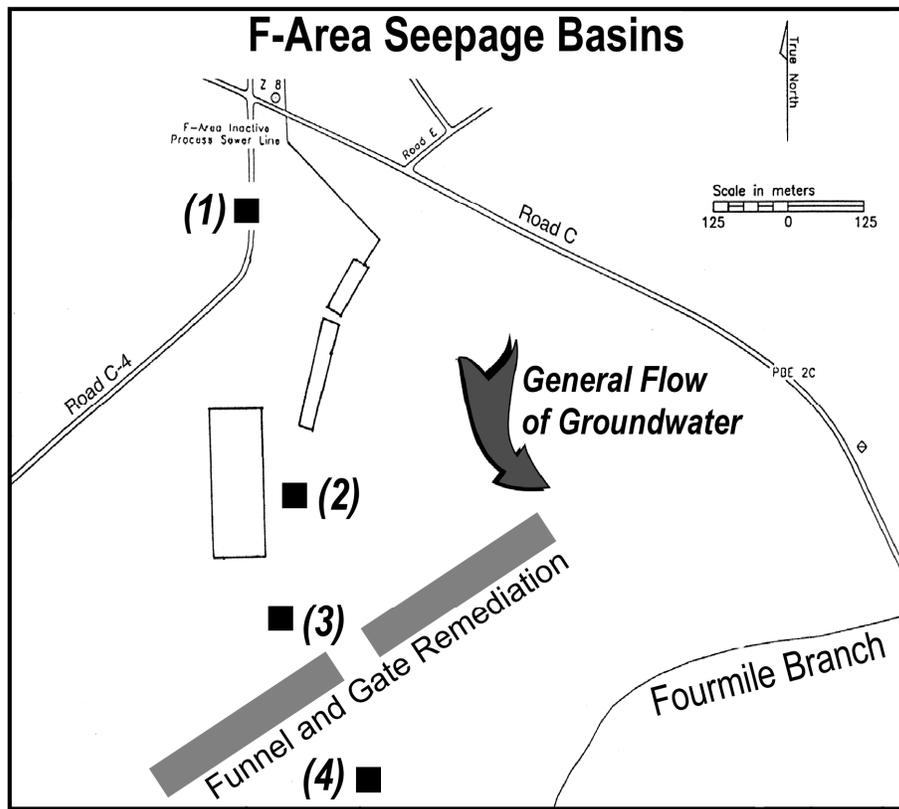
#### **Methods-**

**On Site Cross-Flow Filtration and Maintaining in situ Groundwater Redox State  
Plutonium Oxidation States**

**Consistency of Results**

#### **References**

**Figure S1.** Location of the four wells sampled in this study. The SRS names for Well ID's 1, 2, 3, and 4 are FSB-108D, FSB-92D, FSB-78, and FSB-79, respectively. Well 1 served as the background well, whereas Wells 2, 3, and 4 were 10, 110, and 700 m, respectively, from the seepage basins. Between the 1998 and 2004 sampling campaigns, a funnel and gate remediation wall was established upstream of Well 4 that periodically received large  $\text{NaCO}_3$  base injections in an effort to reduce metal and radionuclide mobility.



**Table S1.** Aqueous Chemistry of Unfiltered Well Water

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<b>Property</b>	<b>Year</b>	<b>Well 1</b>	<b>Well 2</b>	<b>Well 3</b>	<b>Well 4</b>
<b>Depth to water (m)</b>	1998 <sup>(a)</sup>	24.3	19.3	19.3	4.7
	2004	25.6	20.2	19.9	5.8
<b>Temp (°C)</b>	1998	24.0	24.0	25.4	22.4
	2004	19.4	21.7	24.6	23.5
<b>pH</b>	1998	6.8	4.0	3.9	4.1
	2004	5.2	3.7	3.5	6.1
<b>Conductivity (µS/cm)</b>	1998	148.7	744	926	856
	2004	42.1	493	606	432
<b>Na (mg/L)</b>	1998	3.3	11.0	6.6	4.1
	2004	2.68	24.2	7.2	31.6
<b>K (mg/L)</b>	1998	0.28	3.60	3.90	1.10
	2004	0.13	0.99	0.36	0.78
<b>Mg (mg/L)</b>	1998	0.5	2.4	3.4	1.3
	2004	0.5	14.2	1.6	2.2
<b>Ca (mg/L)</b>	1998	4.7	2.9	3.7	2.6
	2004	3.0	17.2	1.2	3.7
<b>Fe (mg/L)</b>	1998	0.009	0.015	0.044	0.239
	2004	0.100	0.127	0.065	0.245

<sup>(a)</sup> The 1998 data was reported in Dai et al. (1)

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## Methods

**On Site Cross-Flow Filtration and Maintaining *in situ* Groundwater Redox State.** In CFF, a prefiltered sample (0.2  $\mu\text{m}$  prefilter used here) solution flows parallel to the CFF membrane. Hydrostatic pressure drives solutes with an effective molecular size less than the cut-off of the membrane (1 kDa), through the membrane (permeate). The remaining solution (retentate) containing both smaller solutes and larger colloids, is swept along the membrane surface and recycled through the retentate reservoir. CFF is applied to environmental sampling with various CFF membrane designs and protocols, resulting in operational differences in the ultrafiltration characteristics (e.g., 2). At a minimum, CFF users need to standardize each CFF system to determine the retention characteristics under field conditions (done here using standard molecules, 1,3) and minimize contamination and sample carry-over by using extensive cleaning protocols. Our CFF blank for Pu was extremely low for this study ( $< 1.2 \times 10^4$  atoms  $\text{kg}^{-1}$  for  $^{239}\text{Pu}$  and  $< 0.6 \times 10^4$  atoms  $\text{kg}^{-1}$  for  $^{240}\text{Pu}$ ). Losses to the CFF system can be evident by mass balance comparisons between the filtered sample and the sum of the permeate and colloidal fractions. The CFF mass balances for the 2004 samples for Wells 2, 3, and 4 were  $100 \pm 3 - 6\%$  for  $^{239}\text{Pu}$ .

Groundwater CFF sampling requires strict redox control since groundwater is generally more reducing than surface waters and our goal is to determine *in situ* speciation of elements that occur in a variety of redox states. Hassellöv et al. (4) demonstrated in other groundwater studies that if redox control had not been maintained, oxidation of reduced Fe in solution can form new Fe oxide colloids and particles that can co-precipitate elements such as Pu, thus changing dramatically the fraction of Pu associated with colloids.

Finally, in one F-area experiment, a groundwater sample was “aged” for 3 days in an open container prior to processing. The main change in Pu speciation was a shift from 38% reduced  $^{239}\text{Pu}$  in the on-site separation filtrate, to only 18% in the aged sample, reflecting the impact of exposure to air (this experiment was conducted only at our most contaminated well, Well 2, but not the most reducing well, where sensitivity to redox control is expected to be larger). This is significant as a delay of several days between sampling and oxidation state separation is common in field studies, and could produce an unacceptable experimental artifact if care is not taken to maintain ambient redox conditions.

**Plutonium Oxidation States.** The redox speciation method separates Pu into Pu(III/IV) and Pu(V/VI) subfractions by a method adapted from Lovett and Nelson (5). The method employed two tracers that are distinguishable isotopically as well as by their oxidation states, so any possible change of oxidation state of the tracers during processing was ultimately revealed by TIMS results, from which, correction factors could be determined (1,6).

**Consistency of Results.** The same groundwater Pu speciation methods as applied in this study have produced comparable, but different results in other settings. For example, differences between  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  were not seen at Hanford 100-K area (6), where there is no evidence of a source dependent control on Pu from the isotopic data or historical releases to suggest a  $^{244}\text{Cm}$  source. That does not mean that Cm would not be found at other DOE sites, such as Oak Ridge where Cm in groundwater is evident (7); however, so far no one has made the direct connection to source dependent controls on  $^{240}\text{Pu}$  at these additional DOE sites where it must similarly be occurring. Also, while the reduced fraction for both Pu isotopes in the F-area filtrate is higher in 2004, it is similar to Hanford K-area, where 65% of the filtrate of both isotopes was reduced. At

Hanford, and more similar to the 2004 SRS data, 10-30% of both isotopes was found associated with colloids (6).

We gained further confidence in our methods by looking at two samples from Pond B at SRS which is known to be contaminated with Pu and other radionuclides (8). In October 2004 we measured a gradient in redox conditions between more oxic surface waters (Eh = 280 mV) and reducing hypolimnion waters (Eh = 30 mV). The percent reduced Pu increased with depth: 70% at 1-m depth and >98% at 8-m depth for both  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . We only have colloidal abundance information from the shallower Pond B sample (as a result of clogging of the cross flow filter), and again it is at the higher end, 40-75% colloidal, and is the same for both isotopes. These higher colloid associations are thus consistent with the more reducing conditions in the pond and show the same behavior for both Pu isotopes in settings where there is no significant  $^{240}\text{Pu}$  derived from Cm decay. These high % colloidal values for Pu are also consistent with other surface waters sampled by similar CFF procedures, such as at Rocky Flats (9).

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